

# Improving Guayule Rubber by Shrub Retting<sup>1</sup>

**W**HEN production of guayule rubber was undertaken by the government in 1942, research was instituted both on production methods and on improvement in quality of the rubber. Among methods bearing on the latter the Spence<sup>2</sup> process was studied. This process, called retting by Spence because of its loose analogy to flax retting, consists in maintaining the shrub in a moist condition in the presence of air for a period of days. Decomposition of the shrub "due to natural agencies"<sup>3</sup> takes place, and then the rubber is extracted by customary mechanical methods. This rubber has a higher tensile strength and lower resin content than rubber from shrub that has not been retted. Records of the Intercontinental Rubber Co.<sup>4</sup> show that the process was tried at its Torreon, Mexico, plant for several months. Great difficulty was encountered in obtaining uniform results, particularly in bulks of 30 to 50 tons. The shrub was piled 10 feet deep in open bins. Although retting took place at the surface, within the mass the shrub did not ferment, at least in the desired manner. Several methods of increasing aeration were tried unsuccessfully. The process was abandoned, probably because there was no overall improvement in the rubber throughout the piles.

Since there are many comments in these records to the effect that shrub in small piles, or around the surface or near air vents in the large piles, did ferment properly and yielded better rubber, we concluded that possibly lack of air was still the limiting factor and decided to study the process from that angle. Our results have borne out this conclusion. Access of air to all parts of the shrub mass is a primary requisite, and if other conditions, such as moisture and temperature, are correct, satisfactory retting takes place, and improved rubber results.

Previous retting work had been done with shrub seven years old or more. Since the government program involved the use of a shorter growing period, it was necessary to ascertain whether two-year-old shrub could be retted satisfactorily. A complete bacteriological and biochemical study of the microorganisms involved in the process has already been reported.<sup>5</sup> The present paper reports the effect of retting on the quality of the rubber recovered from the retted shrub. A study of resin digestion by organisms isolated during these experiments has also been reported.<sup>6</sup>

## Equipment and Methods

The retting tank was fully described, with a diagram, in a previous paper.<sup>5</sup> It was 2½ feet in diameter and four feet high, with four-mesh wire false bottom and facilities for controlling water temperature, air flow through a sparger [sprinkler] in the bottom, and circulation of bottom liquor over the retting shrub. In addition to an electric heater for maintaining the temperature of the liquor, steam could be passed through the air sparger for rapid heating when necessary.

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Air-dried two-year guayule shrub was defoliated, cut to two-inch lengths in a rotary knife cutter, and crushed to ½- to ¼-inch thickness in a cane mill. For chemical analysis the prepared shrub was riffled to a 1% to 2% sample, which was cut to pass a 1/16-inch screen and further riffled if necessary. Moisture, benzene-soluble (rubber hydrocarbon), and acetone-soluble contents ("resin") were determined, the latter two by a modification of the Spence-Caldwell procedure.<sup>7</sup> All analyses except moisture are reported on a moisture-free basis.

Shrub of known weight was placed in the tank and hydrated either by boiling and cooling or by frequent spraying with warm water. It was then maintained in a moist condition, without inoculation, with slow ingress of warmed and humidified air into the tank. The rate of air flow was 10 cubic feet per hour for the first three experiments described below, corresponding to approximately two changes of air per hour. The temperature of the shrub was controlled by spraying with retting liquor. After a suitable interval the entire mass was removed, weighed, and mixed. A sample was then taken for recovery of the rubber by milling, and the residue was returned to the tank for continued retting.

The sample was cut wet in a rotary knife cutter to pass through a ½-inch screen, grab-sampled for analysis, and subjected to a standard pebble-milling procedure for recovery of rubber. The crude rubber obtained was dried in vacuum and compounded according to the following formula:

	Parts	Mill temperature, 115° F. Cure temperature, 274° F.
Crude rubber .....	100	
Captax .....	1	
Zinc oxide .....	5	
Stearic acid .....	1.5	
Sulphur .....	3.5	

Test sheets four by four inches by 0.03-inch in size were used. Observations in this laboratory indicate that sheets of this thickness give results about 300 p.s.i. higher than the standard thickness. This does not invalidate the results, since the data here are all relative.

## Effect of Temperature of Retting

The first major variable studied was the temperature of the fermentation. Three ranges were selected, 95-100°, 107-118°, and 122-129° F. Shrub used in these experiments was preboiled 30 minutes in an effort to hasten decomposition. Such treatment should remove soluble substances, hydrate, and soften the tissue to permit easier

<sup>1</sup> "Natural Rubber from Domestic Sources." Paper No. 5.

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<sup>3</sup> D. Spence, U. S. patent No. 1,918,671 (1933).

<sup>4</sup> Private communication.

<sup>5</sup> J. Naghski, J. W. White, Jr., and Sam R. Hoover, *J. Bact.*, 48, 159-78 (1944).

<sup>6</sup> P. J. Allen, J. Naghski, and Sam R. Hoover, *Ibid.*, 47, 559-72 (1944).

<sup>7</sup> C. O. Willits, W. L. Porter, and C. L. Ogg (in preparation).

penetration by the microorganisms and make for a more selected residual microflora.

The effect of the temperature of retting on the composition of the shrub is shown in Table 1. There was no apparent difference in percentage of resin (acetone extract) in the shrub. Decomposition of the resin fraction of the shrub occurred, however, as is evident when the resin content is considered on the original dry-weight basis. The increase in rubber hydrocarbon content was proportional to the dry-weight loss. No significant loss of rubber hydrocarbon to the liquor occurred. Excellent rubber "balances" at the beginning and end of the experiments showed that no decomposition of rubber took place under these conditions, although ZoBell and Grant found that many bacteria could oxidize rubber under certain conditions.<sup>8</sup>

TABLE 1. EFFECT OF TEMPERATURE OF RETTING ON THE COMPOSITION OF PREBOILED SHRUB

Time Retted Days	Moisture %	Resin %	Rubber Hydrocarbon %	Loss of Dry Matter, Cumulative %
Retted at 95-100° F. (U24S4)*				
0†	14.1	6.1	7.5	0
0‡	12.0	6.6	8.9	13.3
4	67.9	6.9	10.3	24.1
8	75.3	7.1	10.9	25.1
Retted at 107-118° F. (U24S3)				
0†	14.1	6.1	7.5	0
0‡	12.0	6.6	8.9	13.3
4	61.0	6.6	10.5	19.3
7	65.9	7.1	11.2	26.6
13	68.7	6.4	11.7	30.3
Retted at 122-129° F. (U24S5)				
0†	18.0	7.2	9.0	0
5	61.1	6.9	11.3	16.9
9	64.4	6.6	11.7	21.2
14	66.3	6.4	12.4	26.2

\* Code numbers correspond to those used previously.<sup>3</sup>

† Not boiled or retted.

‡ Boiled, but not retted; dried before milling.

TABLE 2. EFFECT OF TEMPERATURE OF RETTING ON THE COMPOSITION OF CRUDE RUBBER MILLED FROM RETTED PREBOILED SHRUB

Time Retted Days	Resin %	Rubber Hydrocarbon %	Insolubles	Ratio of Resin to Rubber
Retted at 95-110° F. (U24S4)				
0*	22.3	64.4	13.2	0.35
0†	23.8	59.8	16.4	0.40
4	19.2	67.1	13.7	0.29
8	16.5	68.9	14.6	0.24
Retted at 107-118° F. (U24S3)				
0*	22.3	64.4	13.2	0.35
0†	23.8	59.8	16.4	0.40
4	19.8	68.7	11.5	0.29
7	19.5	66.9	13.6	0.29
13	15.1	72.5	12.7	0.21
Retted at 122-129° F. (U24S5)				
5	19.9	68.4	11.7	0.29
9	18.8	69.3	11.9	0.27
14	17.0	72.5	10.5	0.23

\* Not boiled or retted.

† Boiled, but not retted.

TABLE 3. TENSILE PROPERTIES OF CRUDE RUBBER MILLED FROM RETTED PREBOILED SHRUB

Time Retted Days	Optimum Cure Minimum	Tensile at Break P.S.I.	Modulus at 600% E. P.S.I.	Ultimate Elongation %	Shore Hardness
Retted at 95-100° F. (U24S4)					
0*	60	1700	460	700	32
0†	45	1740	1380	630	39
4	45	1610	550	760	40
8	30	1840	800	780	45
Retted at 107-118° F. (U24S3)					
0*	60	1700	460	700	32
0†	45	1740	1380	630	39
4	30	2470	870	730	40
7	30	2400	1240	720	40
13	45	2340	1480	690	47
Retted at 122-129° F. (U24S5)					
5	20	2510	820	820	42
9	45	2360	830	730	45
14	60	2370	770	760	38

\* Not boiled or retted.

† Boiled, but not retted.

Samples from each ret were milled, and the crude rubber "worms" were boiled at atmospheric pressure to

cause bits of floating bagasse to sink. AgeRite Powder antioxidant was added to the mill in each case. Analytical data on the crude rubber from the experiments outlined in Table 1 are given in Table 2, and results of physical tests on the vulcanized rubber are given in Table 3.

Results of the temperature series show little or no analytical differences between the three experiments, except that in the 95-100° experiment higher insoluble content was found in the rubber. Table 3, however, shows that only in the 107-118° and 122-129° rets were there any significant improvement in the physical properties of the rubber. The poor result in the 95-100° fermentation might be due to greater frequency of spraying, resorted to in order to maintain the lower temperature. This waterlogged the mass and interfered with proper retting.

### Retting of Unboiled Shrub

Table 3 also shows that no further increase in tensile value of rubber from retted boiled shrub occurred after about four to seven days. Previous small-scale experiments had shown that in the retting of unboiled shrub tensile values continued to increase up to 22 days, with a corresponding decrease in acetone extracts, although disintegration of the plant tissue was less than that in boiled shrub. Furthermore boiling facilitated softening of the tissue during retting to such an extent that undue packing resulted, forming areas less pervious to air. For these reasons subsequent experiments were carried out on unboiled shrub.

Since no definite effect of temperature of retting was observed in the previous three experiments, except that the low temperature was undesirable, the temperature was allowed to range from 107° to 122° F. Sufficient shrub for two millings was retted, and the millings were made at four and eight days. The shrub was hydrated by 12 five-minute circulations of the liquor the first day. Analyses of the retted shrub and of the recovered rubber are presented in Table 4, and results of physical tests of the rubber in Table 5.

TABLE 4. COMPOSITION OF RETTED UNBOILED SHRUB AND OF RUBBER MILLED FROM IT

Time Retted Days	Moisture %	Resin %	Rubber Hydrocarbon %	Insolubles %	Loss of Dry Matter, Cumulative %
Unboiled Retted Shrub (U24S6)					
0*	39.9	7.5	9.3	...	0
4	61.1	7.1	10.1	...	14.0
8	63.6	6.3	10.4	...	16.6
Crude Rubber Milled from Unboiled Retted Shrub					
0*	...	19.4	69.1	11.4	...
4	...	20.1	68.4	11.5	...
8	...	18.3	71.2	10.5	...

\* Control analyses for a different, but comparable lot of material are given.

TABLE 5. TENSILE PROPERTIES OF CRUDE RUBBER MILLED FROM RETTED UNBOILED SHRUB

Time Retted Days	Optimum Cure Minimum	Tensile at Break P.S.I.	Modulus at 600% E. P.S.I.	Ultimate Elongation %	Shore Hardness
0*	45	2260	510	830	29
4	30	2340	610	810	41
8	30	2610	520	840	43

\* See footnote, Table 4.

Comparison of Tables 4 and 5 with Tables 1, 2 and 3 shows that although the composition of the crude rubber from the unboiled shrub was similar to that obtained from the boiled shrub, the tensile values indicated a different trend with time of retting. In this case the maximum tensile strength was not passed at about four days but there was a continued increase to at least eight days

With this in mind the next experiment was planned to run for 21 days.

Because of limited raw material, the quantities retted in the previous four experiments were sufficient to fill the retting tank only to a depth of about 20 inches. As previously noted, the difficulty encountered by the Intercontinental Rubber Co. was in obtaining uniform retting throughout a large bulk of material. Enough shrub to fill the tank completely was used in the next two experiments, giving a shrub depth of three feet. Furthermore, a drum of water (total weight, 570 pounds) was placed on top of the sparger to simulate the packing effect of the weight of an additional 2.2 feet of wet shrub. The rate of aeration was increased to 100 cubic feet per hour, or 6.5 changes per hour.

At the end of seven days' retting the tank was emptied, and samples of shrub were removed for milling as follows: first, top two inches; second, center of the bulk; third, remainder (well mixed). Enough shrub for two

milling batches was taken from the mixed bulk and returned to the tank for further retting, and representative samples were removed at 14 and 21 days. The results of the experiment are shown in Tables 6, 7, and 8.

Comparison of the data in Tables 6, 7, and 8 with the results Spence<sup>3</sup> obtained by retting in shallow layers reveals excellent agreement. Results in Table 8 show that retting occurred throughout the mass, although at a slightly slower rate in the center than at the top. Our fermentation was not carried beyond 21 days, since it was felt that this represented the commercially feasible time limit. Figure 1, based on the data in Tables 7 and 8, shows close interrelation between retting time, resin content, tensile strength, and rubber hydrocarbon content. Walter<sup>9</sup> found no qualitative differences in the constituents isolated from the resin of retted and unretted guayule in these experiments.

<sup>9</sup> E. D. Walter, *J. Am. Chem. Soc.*, 66, 419-21 (1944).

TABLE 6. COMPOSITIONS OF UNBOILED SHRUB (U24S7) RETTED IN BULK

Time Retted Days	Description	Moisture %	Resin %	Rubber Hydrocarbon %	Loss of Dry Matter, Cumulative %
0	Control	13.0	6.3	7.1	0
7	Bulk	60.5	6.8	8.4	18.6
7	Center	66.6	7.3	9.0	...
7	Top	65.5	6.2	8.6	...
14	Bulk	67.2	5.7	8.9	23.6
21	Bulk	69.3	5.8	9.4	29.4

TABLE 7. COMPOSITION OF CRUDE RUBBER FROM UNBOILED SHRUB (U24S7) RETTED IN BULK

Time Retted Days	Description	Resin %	Rubber Hydrocarbon %	Insolubles %	Ratio of Resin to Rubber
0	Control	22.7	66.0	11.3	0.34
7	Bulk	18.0	71.9	10.1	0.25
7	Center	22.3	67.9	9.8	0.33
7	Top	19.6	70.0	10.4	0.28
14	Bulk	15.1	74.4	9.5	0.20
21	Bulk	13.5	77.2	9.3	0.17

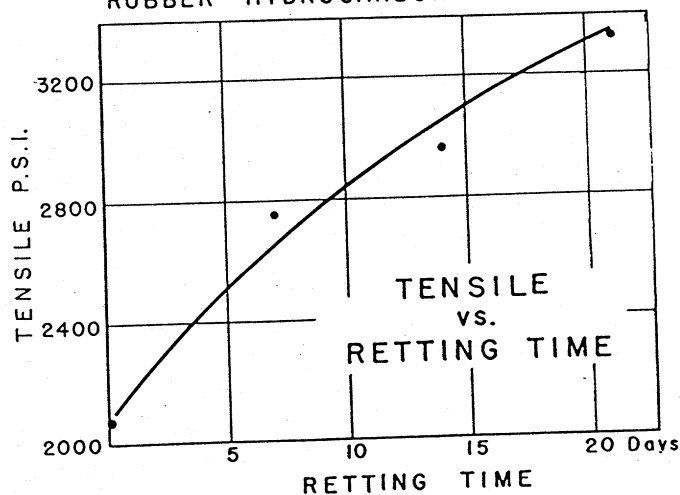
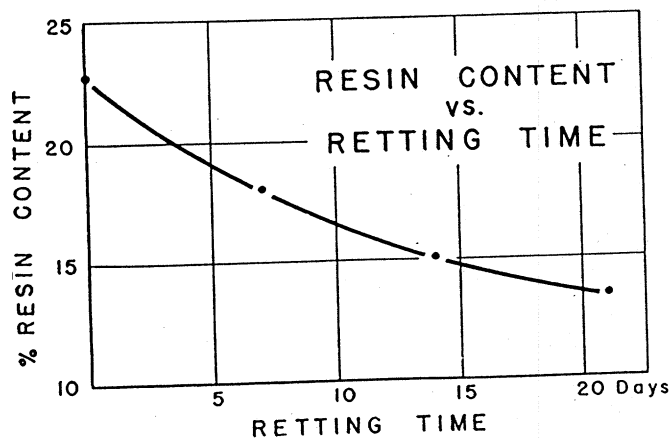
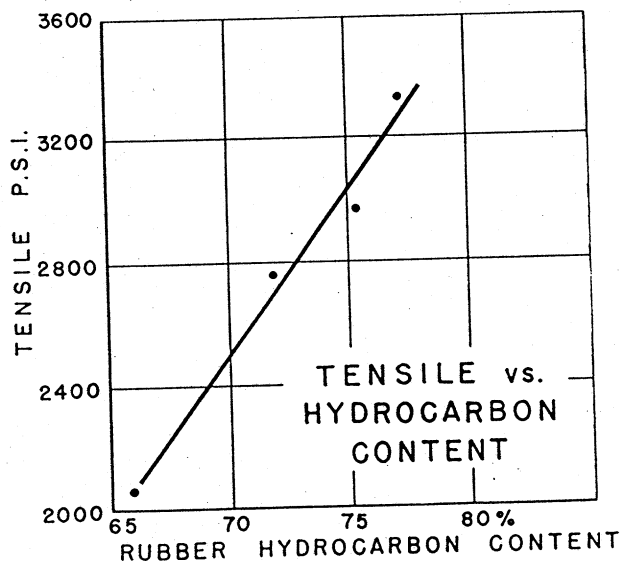
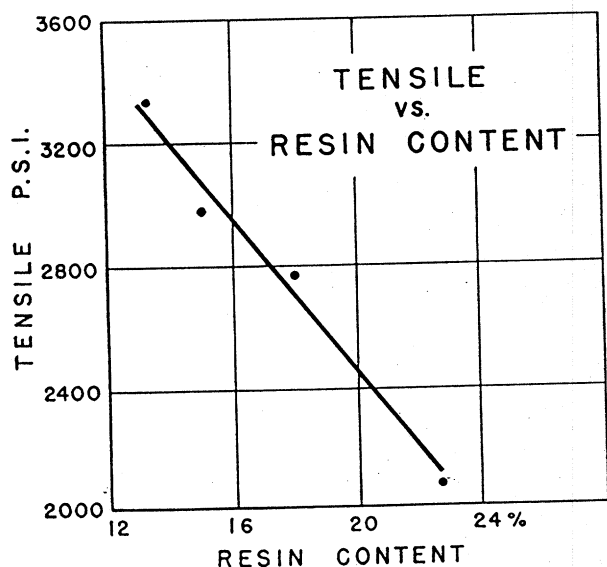


Fig. 1. Effect of Shrub Retting on Guayule Rubber

TABLE 8. TENSILE ~~STRENGTH~~ ~~OF~~ RUBBER FROM UNBOILED SHRUB ~~RETING~~ ~~IN~~ BULK

Time Retted Days	Descriptions	Tensile Break P.S.I.	Modulus 600% E. P.S.I.	Ultimate Elongation %	Shore Hardness
0	Control	2571	530	800	44
		2551	570	790	46
		1771	640	740	47
		1551	640	730	47
		1591	650	730	48
1	Bulk	2551	480	860	37
		731	630	810	39
		1551	630	800	40
		711	710	790	40
		1551	630	750	40
7	Center	2551	500	850	27
		2501	710	800	33
		221	950	780	36
		2551	950	730	37
		271	1120	710	36
7	Top	2551	560	850	33
		2551	630	820	36
		2551	760	800	37
		2551	840	780	37
		2551	870	760	38
11	Bulk	2551	280	860	32
		2551	500	840	30
		2551	510	810	32
		2551	490	820	35
		2551	460	910	37
21	Bulk	2551	570	860	38
		2551	600	840	38
		2551	560	840	40
		2551	580	850	42
		2551	580	850	42

\* Optimum

The final ~~strength~~ ~~of~~ ~~the~~ ~~one~~ ~~last~~ ~~described~~ ~~from~~ ~~1920~~ ~~to~~ ~~3050~~ ~~p.s.i.~~ ~~was~~ ~~obtained~~ ~~from~~ ~~the~~ ~~resin~~ ~~content~~ ~~from~~ ~~20.6~~ ~~to~~ ~~12.3%~~.

The ~~improvement~~ ~~shown~~ ~~by~~ ~~rubber~~ ~~from~~ ~~retted~~ ~~guayule~~ ~~reflect~~ ~~the~~ ~~improved~~ ~~compounding~~ ~~of~~ ~~the~~ ~~rubber~~. It is also possible that the ~~retted~~ ~~rubber~~ ~~of~~ ~~microbiological~~ ~~fermentation~~ ~~may~~ ~~contribute~~ ~~to~~ ~~the~~ ~~better~~ ~~retting~~. There is no reason to believe

that an improvement is made in the quality of the actual rubber hydrocarbon itself.

Consideration of the data shows that, as is usual in biological processes, there is an interrelation among temperature, oxygen supply, time, and water content. Therefore the conditions for retting cannot be defined in terms of any one of these requirements, nor indeed can successful retting be carried out if any one of these is not controlled.

Further laboratory and pilot plant investigations are being carried out by the Guayule Rubber Extraction Research Unit of the Bureau of Agricultural and Industrial Chemistry, Salinas, Calif.

### Summary

1. Forced aeration made it possible to ret guayule shrub under packing conditions equivalent to a depth of at least 5.2 feet. This aerobic retting improved the properties of the rubber, in confirmation and extension of the results obtained by Spence, who did not use forced aeration.
2. Under the conditions employed (adequate aeration, 60 to 70% moisture, and 104° to 129° F.) about 1200-p.s.i. improvement in tensile strength of guayule rubber was obtained by retting the shrub for 21 days, with proportionately less increase in shorter time.
3. The resin content of the recovered rubber was reduced from 20-23 to 12.3-13.5% by the process.

### Acknowledgment

The cooperation of the Chemical Engineering and Development Division in the preparation and milling of the shrub, and of the Analytical and Physical Chemistry Division in the analysis and physical testing of the rubber, is gratefully acknowledged. The authors also take pleasure in acknowledging the technical assistance of Nancy O'Connell Buck, of this Laboratory.